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T H E S I S

PART I

REDUCTION OF VISCOSITY AND GRAVITY OF ALBERTA
BITUMEN BY THERMAL TREATMENT

PART II

THE OXIDATION OF THE PARAFFIN HYDROCARBONS

by

W. S. PETERSON

Edmonton, Alberta.

April, 1944

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REDUCTION OF VISCOSITY AND GRAVITY OF ALBERTA
BITUMEN BY THERMAL TREATMENT

PART II

THE OXIDATION OF THE PARAFFIN HYDROCARBONS

Submitted in Partial Fulfilment
of the
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Master of Science

by

W. S. Peterson

Under the Direction of

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University of Alberta,
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PART I

REDUCTION OF VISCOSITY AND GRAVITY OF ALBERTA

BITUMEN BY THERMAL TREATMENT

INTRODUCTION

The Province of Alberta contains great stores of natural resources many of which await development, either in the economic or the chemical sense, or both. Among such resources are the hydrocarbons which exist in abundance as coal, natural gas and oil and also as bitumen saturating the McMurray sandstone formation in the Lower Cretaceous rocks.

These bituminous sands, or more commonly tar-sands, underlie thousands of square miles in Northern Alberta mainly along the Athabasca River. The deposits vary widely with respect to thickness, concentration, quality and amount of overburden. Relatively little work has been done to develop these areas. This may be due to several factors such as, the lack of detailed knowledge, the difficulty of mining the bituminous sand and the uncertainty with regard to treating processes. However, treating of the bitumen after separation from the sand could probably be done by standard modern refinery practices. Another and probably most important contributing factor to slow development is the lack of market for the bitumen and its products.

The current apparent state of petroleum reserves, whereby new discoveries fail to equal consumption, has stimulated wide interest in the bituminous sands as a

petroleum reserve. The amounts of bitumen available, granted that methods of exploration of the sands can be derived, is extremely large and comparable to petroleum requirements of this continent for a generation.

The Abasand extraction process⁽⁴⁾ results in a mixture containing about 50 percent bitumen and the rest equal volumes of sand and water. To separate the bitumen from sand and water a volume of diluent equal to, or greater than, that of the bitumen-sand-water pulp is added. The diluent is a gas-oil fraction produced in subsequent refining. However, the sand separated in this process contains 20 percent diluent and 20 percent bitumen, basis dry weight. This is recycled in the plant, being subjected to the separational process again. This results in the evaporation and loss of all, or a major part of the diluent associated with the separated sand and bitumen being recycled. This is not the only uneconomical part of the process, for it is estimated that the circulated bitumen represents about 40 percent of the fresh bitumen introduced as bituminous sands.

The difficulties associated with the Abasand process may be eliminated by development of the separation process developed by K. A. Clark⁽⁴⁾. In this relatively simple hot water separation process a mixture of bitumen

with less water and sand is obtained. The water might be separated by electrostatic means. The product of the Clark process is compared to the Abasand process, nearly pure bitumen, and to handle such material by means common in refinery processes introduces difficulties. Some means of producing a less viscous material or synthetic petroleum from the bitumen is desired.

A reduction in viscosity of bitumen may be obtained by coking it at or near atmospheric pressure, thus getting a liquid which is relatively easy to handle and leaving a coke mixture with sand. An alternative to this method, and probably more satisfactory from the standpoint of coke formation, would be the reduction of viscosity by a thermal treatment or "viscosity-breaking" operation. The problem is not very different from the problem of handling residual oils in the petroleum industry.

It is with viscosity breaking of bitumen that this research is concerned. The technical term commonly used is vis-breaking.

THEORETICAL AND LITERATURE REVIEW

Abraham⁽¹⁾ states: "Bitumen is a generic term applied to native substances of variable color, hardness and volatility; composed of hydrocarbons substantially free from oxygenated bodies; sometimes associated with mineral matter and nonmineral constituents, being fusible and largely soluble in carbon disulphide; and whose distillate fractioned between 300° and 350°C yields considerable sulphonation residue".

The bituminous sands of Alberta yield a bitumen which is variable in composition. However, an idea of the ultimate analysis may be obtained from the following⁽⁵⁾:

Carbon	84.5%	Sulphur	2.7 %
Hydrogen	11.2%	Nitrogen	0.04%

For comparison and showing variability of bitumen with the location of sampling the following analysis was found by Boomer and Saddington⁽³⁾:

Carbon	82.3%	Sulphur	4.2 %
Hydrogen	10.2%	Nitrogen	0.37%

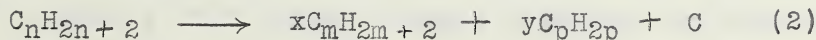
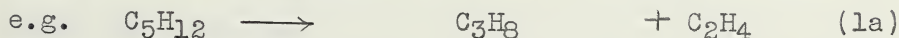
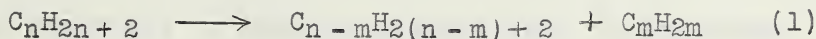
The balance is made up of a small amount of oxygen and mineral matter.

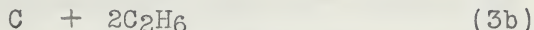
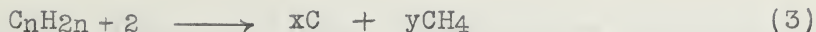
Vis-breaking has long been a standard practice in refineries as a method of reducing viscosity of heavy crude oils and residuums. It is carried out in the liquid phase under mild cracking conditions. These mild cracking

conditions involve a moderately low temperature and pressure and a short time of contact. The long paraffinic side chains of aromatic and hydroaromatic hydrocarbons are split off with the formation of lighter fractions. Depending on the feed material and conditions of temperature and pressure, carbon formation may be absent or slight in amount. The oil resulting from vis-breaking has a lower viscosity than the original feed stock.

Because vis-breaking is a mild cracking operation, the general chemical reactions involved will be the same as those occurring in the primary stages of cracking. The classes of hydrocarbons arranged in their importance in cracking are: the paraffins (as such or as side chains), the olefins (unsaturates), the naphthenes and the aromatics.

The chief reaction of the paraffins is a splitting decomposition yielding lower paraffins, olefins, carbon and small amounts of hydrogen. These products may be derived as in the following equations as proposed by Sachanen (6):

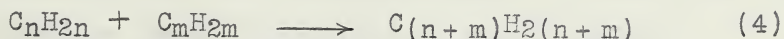




Equation (1) shows the formation of a lower paraffin and an olefin. Equation (2) shows the paraffin decomposing to give a lower paraffin, an olefin and carbon. The paraffin may also yield a non-condensable gas such as methane or ethane along with coke as in equation (3). The first two equations are the more probable of the three reactions for long paraffin chains.

Alkylation of paraffins may occur at low temperatures, but a catalyst is usually required. This reaction is illustrated as the reverse of equation (1) above. Isomerization and aromatic cyclization may also take place, but neither is important in vis-breaking.

In the first stages of cracking, olefins may polymerize to form longer chains, as in equation (4):



Other reactions of olefins occur mainly in the later stages of cracking.

Most of the highly viscous fractions in petroleum are comprised of naphthenes with long side chains of a paraffinic nature. There may be as many as fifteen carbon

atoms in a chain, and these compounds are thermally unstable. It is the cracking of these side chains, or dealkylation of the compound, that is mainly responsible for the "breaking" of the viscosity. Equations (1) to (3) inclusive, illustrate the main reactions occurring in the side chains of aromatic and naphthenic ring compounds. Other reactions besides the dealkylation of naphthenes, are the dehydrogenation to an aromatic compound and isomerization, but these are relatively unimportant here.

Aromatics with side chains may undergo similar reactions. Aromatics, however, alkylate more easily than do either the paraffins or the naphthenes.

Sulphur compounds such as sulphides and disulphides may decompose to hydrogen sulphide and thus reduce the sulphur content of the oil. Mercaptans in later stages of cracking may form hydrogen sulphide and olefins but the reaction is not important to vis-breaking.

Resins and asphaltenes, characteristic constituents of bitumen, are polycyclic compounds which contain sulphur and oxygen as bridges between rings and on side chains. Cracking of these structures yields gases, liquids and much coke.

It is seen from this discussion that there are many different reactions that contribute to viscosity breaking.

There is little definite information on viscosity breaking in the literature. In selective cracking processes⁽⁶⁾, vis-breaking is carried on at about 475°C for a short time to ensure little or no coke formation. A pressure of 200-500 pounds per square inch gauge, great enough to keep most of the product in the liquid phase, is used.

In a combination selective Kellogg cracking unit of the Atlantic Refining Company the reduced crude oil is cracked at about 466°C, measured at the outlet of the vis-breaking coil⁽⁷⁾.

No times are given for these processes, but it would vary considerably with the type of crude oil used and must be determined by experience.

MATERIALS

The bitumen used in this research was recovered from diluted crude bitumen supplied by Dr. K. A. Clark and obtained originally from Abasand Oils Ltd. Four lots of diluted crude bitumen were distilled to remove diluent and the residues were heated and mixed together to give a homogeneous batch. This process of distillation removed any water present. The principal properties of the resulting bitumen are as follows:

Saybolt Furol Viscosity at 122°F	835 sec.
Density at 25°C	1.009
Initial boiling point at 1 cm. pressure	97°C
Suspended Carbon	0%
Sulphur	3.92%

This material is very definitely not the same as the virgin bitumen. The distillation for separation of diluent must inevitably cause changes in the bitumen which is highly temperature sensitive. Further, the boiling range of the diluent and bitumen overlap to some extent. However for purpose of this work, the material is assumed suitable in being not very different from virgin bitumen. Vis-breaking on this altered bitumen, if successful, could be adapted to virgin bitumen.

The natural gas used was from the Viking-Kinsella field. This gas is dry, contains a little sulphur odorant and is high in methane. It was stored under high pressure.

APPARATUS AND ANALYTICAL PROCEDURE

The apparatus for viscosity breaking, which is shown in Figure 1, consists of a means of pumping the oil through a hot tube under pressure, into a large receiver where it was cooled rapidly.

A six cylinder, single action, Madison-Kipp Lubricator, Model 50, was used to pump the bitumen into the manifold, A. An electric heater held bitumen in the pump and manifold at a temperature of 60° to 70°C. The manifold was fitted at one end with a safety valve, E, set to work at about 1,500 pounds per square inch, and at the other end the manifold fed into the reaction tube, B. This tube was made of 18-8 chrome-nickel stainless steel and had dimensions 1/4" I.D. x 7/8" O.D. x 29" long. It had seven thermocouple wells 3/32" diameter x 5/32" deep drilled at the various positions shown in Figure 1. A high pressure valve, D, situated between the manifold and the reaction tube, served as a gas inlet.

The reaction tube was heated by a series of three electric furnaces, F; the first half of furnace #1 acting as a preheater for the bitumen. The reaction tube terminated in a 1/3 gallon pressure bottle, C, acting as product receiver. At the top of this receiver a Bourdon type gauge, G, registered the pressure and the valve, H, was adjusted from time to time during an experiment keep-

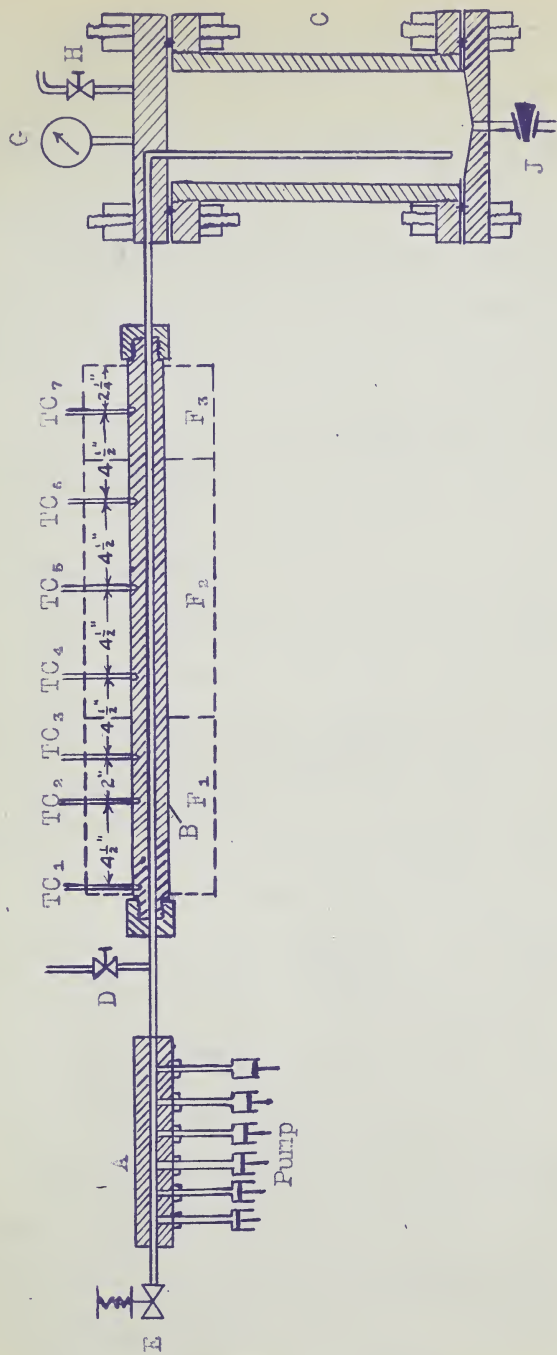


Figure 1 - Visbreaking apparatus

ing the pressure constant. The oil was blown from the receiver at the end of a run through a $\frac{1}{4}$ " plug valve, J, located on a copper tube leaving the dished bottom of the pressure bottle.

Temperature of the various sections of the reaction tube were recorded by a recording potentiometer. Iron-constantan thermocouples were used and were insulated from the tube at the hot junction by a coating of alundum-water glass cement.

Distillation Methods

The diluted crude bitumen as supplied contained better than 50 percent diluent. This was removed in a five-gallon steel still, the cover of which was fitted with a short column 2" diameter and 6" long. The column was not packed and little fractionation occurred. The temperature of the vapor was measured with a thermometer inserted at the top of the short column. A thermometer well penetrated the cover plate of the still into the liquid in order that the still temperature could be taken. The still was heated by a gas burner.

Removal of the diluent was assumed complete when the vapor temperature reached 275°C. The initial boiling point of the diluent was about 160°C and the final boiling point was about 275°C.

Distillations were carried out on the reduced bitumen, as prepared above, and also on the cracked product at the completion of a run. The distillation of cracked bitumen was started at atmospheric pressure if much cracking to volatile products had occurred as indicated by a change in viscosity. When the vapor temperature at atmospheric pressure reached the cracking range, the pressure in the column was reduced to ten millimeters of mercury, and the distillation was continued to the end at this pressure.

The distillation equipment, of glass, is shown in Figure 2. It consisted of a one-litre, round-bottomed flask, A, with a short insulated column, B, 1" diameter x 5" long. The column contained no packing but had an extended surface produced by alternate hemispherical depressions and points in the walls. The vapors were liquefied by a water condenser, C, attached to the side arm and the condensate (distillate) was caught in a graduated receiver, D. Vacuum, under automatic control, was applied through the tube E, just above the receiver. Temperatures of vapor and liquid were measured by means of iron-constantan thermocouples located in a well carried by the ground glass cap of the column. When carrying out a distillation, the heat was adjusted to

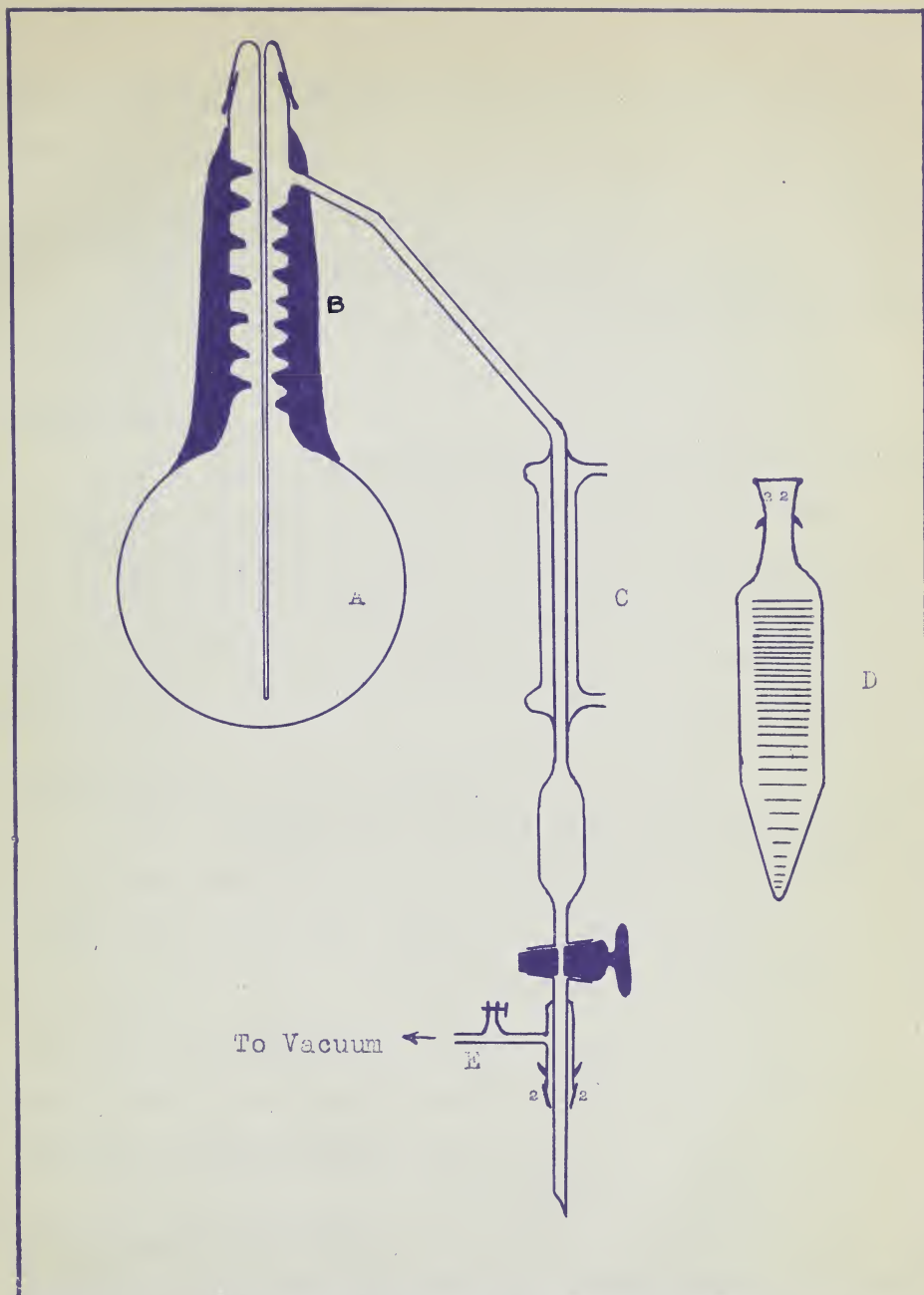


Figure 2 - Vacuum Distillation Apparatus

give a rapid and constant rate of production of condensate.

Viscosity Methods

The viscosity was determined in a Saybolt Furol Viscometer according to A.S.T.M. specifications at 122°F.

Density Method

The density determination was carried out at 25°C on degassed samples in a Hubbard density bottle with a volume 28.99 ml. The bottle and sample were held in a water bath kept at $25^{\circ}\text{C} \pm 0.02^{\circ}$, until the bitumen had come to the temperature of the bath.

Suspended Carbon Determination

The bitumen, or reamings from the reaction tube, or residue from the receiver was dissolved in benzene or carbon disulphide and filtered through a gooch crucible. The residue on the filter was washed thoroughly with the solvent, dried at 110°C, weighed, ignited to burn off carbon, and then weighed again. The loss in weight was assumed to be suspended carbon.

Sulphur determination

The sulphur content was determined by the method of Boomer and Saddington(2). Briefly, the bitumen was heated slowly in a quartz combustion tube with a brisk

current of air passing over it. Platinum wire at 900°C catalysed the oxidation. The temperature of the bitumen was raised slowly and steadily until completely oxidized. The off-gas was washed by a known volume of standard sodium carbonate solution in a fritted glass scrubber. Finally the solution was titrated with standard hydrochloric acid and the amount of sulphur in the oil (bitumen) sample computed.

Other Determinations

The volume of the bitumen charge was taken as the weight of material recovered from the receiver divided by the density of the original bitumen. The time of contact was determined from the volume of the reactor, the time taken for a run and the volume of the cracked product. Neither figure is very exact. Losses of bitumen in the form of gas, coke and liquid wetting equipment surfaces occurred. These losses are probably of the order of 1% of the total.

Operating Procedure

The pump and its reservoir were filled with bitumen and the heater under the pump was turned on. The furnaces were turned on at the same time and the rheostats set to give approximately correct temperatures. After four or five hours, when the temperatures had been adjusted

precisely and had steadied, the experiment was started. In setting the furnace temperatures, account had to be taken of the cooling effect of the bitumen when flowing in the tube. This amounted to 50-100°C for the first furnace and 15-30° for the rest of the furnaces.

The pump and stopwatch were started together. Immediately, the pressure was raised to the desired value from the high pressure gas source. The preheating furnace (#1) rheostat was then turned to full heat. The temperatures along the reaction tube were watched closely and kept as constant as possible. The valve H, Figure 1, was adjusted so as to keep the pressure constant.

After 350 ml. or more of bitumen had passed through the reaction tube, the pump and stopwatch were stopped together. The leak valve, H, was opened more and the oil remaining in the tube was blown into the receiver by gas from the high pressure line entering through valve D, Figure 1. The heater and furnaces were then shut off.

The cracked product was blown out of the receiver into a wide-mouth erlenmeyer flask and weighed. Before viscosity and density were determined the oil was degassed by warming until fluid. This caused the bubbles of gas on the oil to separate and leave a homogeneous liquid. To minimize loss of light fractions overheating was avoided on products that had been cracked to a considerable extent.

RESULTS AND DISCUSSION

Effect of Temperature

In considering the effect of temperature, while the qualitative trend is obvious, Table I, a great deal of uncertainty exists as to what is the real temperature of the oil. The indicated temperature changed with time during an experiment and further, changed relatively along the tube. Finally, the oil temperature is not the same as the thermocouple temperatures but is related to the thermocouple temperatures in a complex way.

Rather than table each temperature and time for each of seven thermocouples an arbitrary method of computing a "characteristic" temperature for each experiment was devised. In setting up the method thermocouple 1 was neglected and temperatures shown by the other thermocouples were averaged in respect to time and the length of the tube. While furnace #1 was considered to be a preheater doubtless reaction took place in the part of the tube enclosed. This is confirmed by coke formation in this part of the tube. To counteract the cooling resulting from the bitumen flow, furnace #1 was generally set at a temperature 40° to 50°C above the rest of the furnaces. This was necessary, otherwise the temperatures in furnaces #2 and #3 fell off very badly, but it did result in furnace #1 producing reaction as well as preheating.

TABLE I. Experimental Data and Results

Experiment No.	Pressure psi.	Saybolt Furol Viscosity sec.	Density 25°C	"Characteristic" Tube Temperature °C	Time of Contact sec.	% Suspended Carbon	% Sulphur
Original Bitumen	-	835	1.009	-	-	0	3.92
1	200	770	1.008	225	8	-	-
2	200	823	1.009	300	17	-	-
3	200	821	1.009	393	18	0.01	-
6	200	77	0.996	494	100	0.5	-
7	200	217	1.003	460	103	small	-
8	200	523	1.004	413	106	-	-
9	200	80	0.997	487	106	0.8	-
10	100	125	1.000	484	98	0.2	3.58
11	400	53	0.994	483	121	0.2	3.35

In computing the "characteristic" temperature, the method is illustrated in what follows by use of a particular experiment Number 8.

The temperatures and times as recorded during the run are given below in Table II for experiment #8.

Table II. Recorded Data for Experiment 8

Time Minutes	Temperature - °C						
	Furnace #1			Furnace #2			Furnace #3
	T.C.1	T.C.2	T.C.3	T.C.4	T.C.5	T.C.6	T.C.7
0	250	495	470	407	440	403	415
5-6		460	470	398	425	400	415
9-11		460	480	360	395	380	409
13-16		460	483	395	397	376	405
18-20		453	475	390	413	398	402
30-32		467	489	391	412	397	402
40-42		465	488	390	413	397	402

The temperatures for each time interval were averaged between thermocouples, 2 and 3, 3 and 4, 4 and 5, etc. For example, in the row 5 to 6 minutes (average time $5\frac{1}{2}$ minutes) the mean temperature between thermocouples 2 and 3 is 465°C . This data is given, together with the time and the thermocouple pair in Table III for experiment #8. The temperatures given in Table III were averaged as between successive times for each column and these averages were multiplied by the time interval corresponding to

Table III. Mean Temperatures Between Thermocouples - Exp. 8

Row	Average Time	Mean Temperature - °C Between					
		T.C. 2&3	T.C. 3&4	T.C. 4&5	T.C. 5&6	T.C. 6&7	T.C. 7&end
I	5½ min.	465	434	412	412	408	415
II	10 "	470	420	374	388	395	409
III	14½ "	471	439	396	387	390	405
IV	19 "	464	433	401	406	400	402
V	31 "	478	440	401	405	399	402
VI	41 "	477	439	402	405	399	402

Total Time Interval - 35½ minutes

each average. For example, the mean temperatures between thermocouples 2 and 3 are 465°C at 5½ minutes and 470°C at 10 minutes (Table III). The mean of these two is 467.5°C which is multiplied by the time interval 4½ minutes, between rows I and II (Table III). This gives a value of 2,104. These time temperature products are shown in Table IV.

Table IV. Time-Temperature Products for Experiment 8

Product Between Row	Time Temperature Products Between					
	T.C.2&3	T.C.3&4	T.C.4&5	T.C.5&6	T.C.6&7	T.C.7&end
I & II	2,104	1,922	1,769	1,800	1,807	1,854
II & III	2,117	1,933	1,733	1,744	1,766	1,832
III & IV	2,104	1,962	1,793	1,784	1,778	1,816
IV & V	5,652	5,238	4,812	4,866	4,794	4,824
V & VI	4,775	4,395	4,015	4,050	3,990	4,020
Sum	16,752	15,450	14,122	14,244	14,135	14,346
Time Average Temp. °C (T.A.T.)	471	435	398	401	398	404
Distance Between T.C.	2"	4½"	4½"	4½"	4½"	2½"
T.A.T. x Dist.	942	1,985	1,791	1,804	1,791	909

Sum of T.A.T. x Distance = 9,195

Total Length - (T.C.2 to end of furnace 3) = 22.25"

Characteristic Temperature - Expt. 8 = 413°C

The sum of each column was divided by the total time interval to yield a kind of time average temperature for each pair of thermocouples.

The last step was to take account of the longitudinal temperature gradient in the reaction tube. The time average temperatures in Table IV were multiplied by the distance in inches between each pair of thermocouples, the resulting products being shown also in Table IV. The sum of these products was divided by the total length of the reaction tube concerned, from thermocouple 2 to the end of furnace

#3, namely 22.25" to give the desired "characteristic" temperature.

Admittedly the computation is arbitrary, but does give a measure of temperature taking into account time and distance variations and should give relative temperatures as between experiments.

A considerable reduction in viscosity was obtained at temperatures from 480° to 500°C. Values of viscosity were obtained that were less than one tenth the viscosity of the original bitumen. The reduction in density was not so pronounced, Figure 3a, but was appreciable.

The effect of temperature on viscosity can be seen plainly in Figure 4. Most of the runs were made at a pressure of 200 pounds per square inch and at a time of contact about 100 seconds. The solid curve, marked 200 psi, Figure 4, represents actual values obtained from experiments # 6-9 inclusive. The viscosity was reduced from the original value of 835 seconds to 70 seconds by vis-breaking at 500°C. The value for viscosity appears to level off above 500°C to a value somewhat below 70 seconds.

Effect of Pressure on Viscosity

At first glance Fig. 3b would tend to give an exaggerated impression of effect of pressure on vis-breaking.

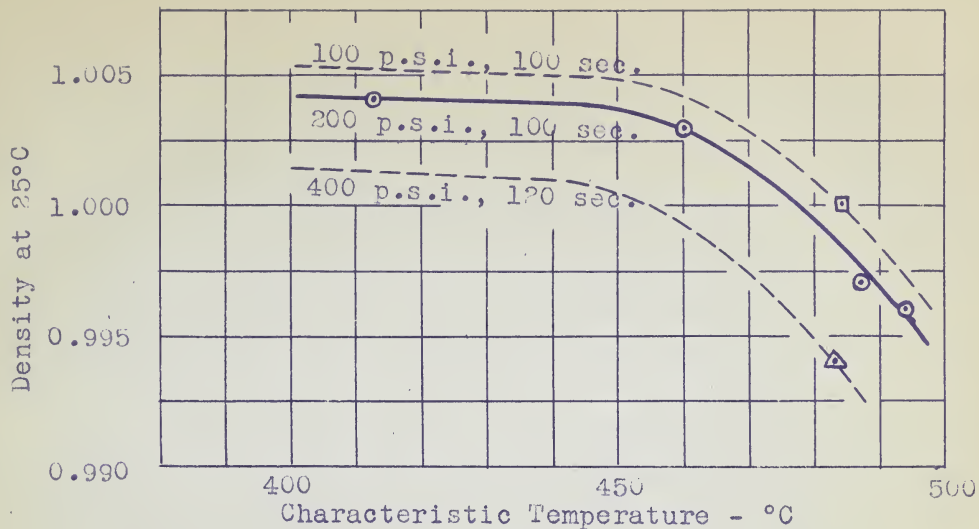


Figure 3(a) - Effect of Temperature on Density

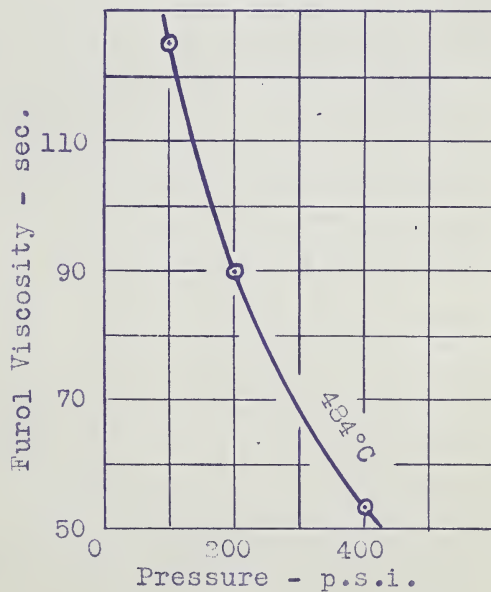


Figure 3(b) - Effect of Pressure on Viscosity

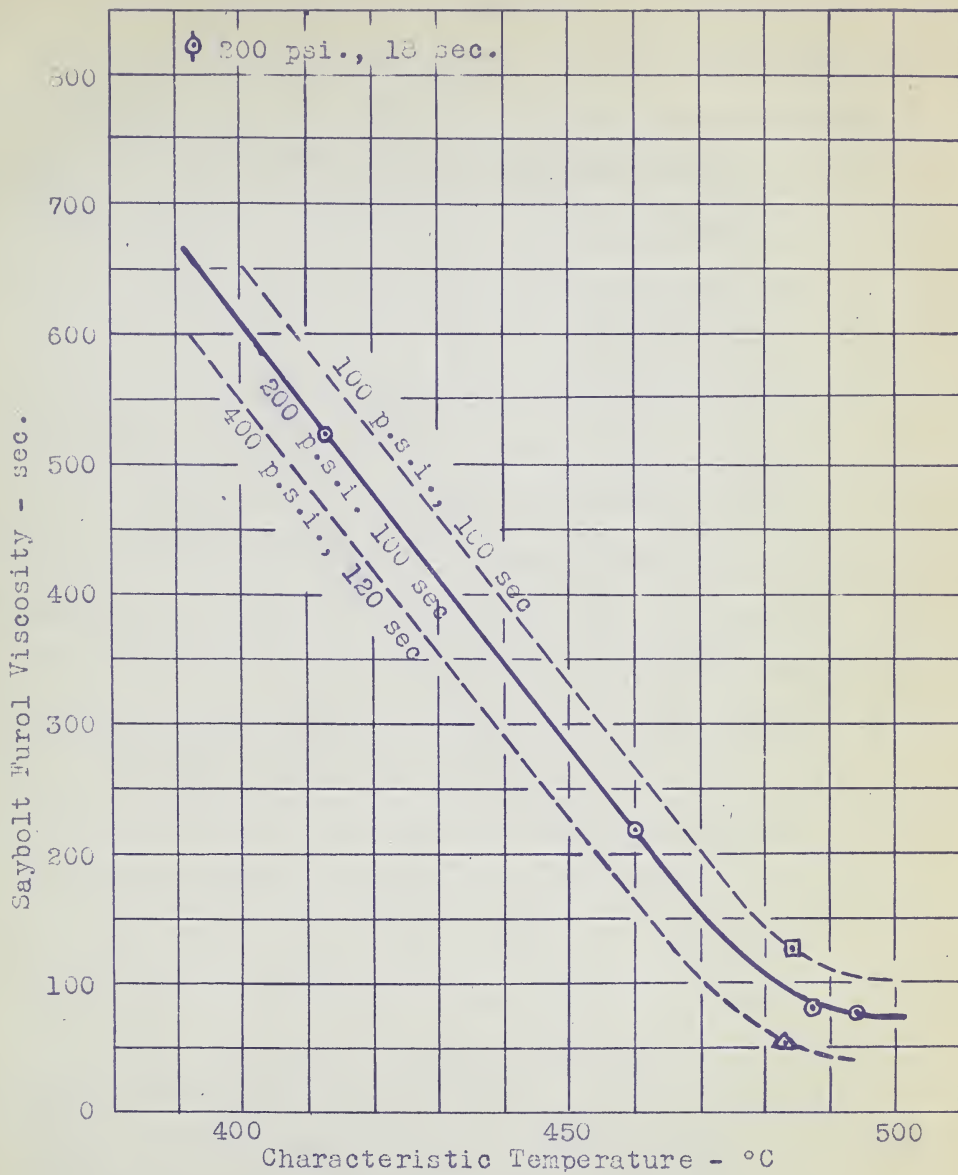


Figure 4 - Effect of Temperature on Viscosity

It is seen that for constant temperature, viscosity decreases rapidly with increase of pressure (see also broken curves, Fig. 4). However this is very misleading because a study of contact times for experiments 10 and 11 (100 and 400 psi, respectively) (Table I) show the time of contact for 100 psi to be much less than for 400 psi (98 seconds and 121 seconds, respectively). This is due to an unexpected limitation of the pump, i.e. at a higher pressure each piston stroke delivers less oil and time of contact is increased accordingly. This increase in time of contact may mask any pressure effect that may exist. However, the data at 100, 200 and 400 psi does suggest improved results at the higher pressure. Further work on the effect of pressure is desirable.

The first stages of cracking is a monomolecular reaction and as such, the velocity constant should be independent, or nearly so, of pressure. This is, of course, only true if the pressure is above the critical pressure of the oil being cracked, and gases are not liberated. From this it may be concluded with reasonable safety that while pressure has an effect, it is less than shown in Figure 3b.

Effect of Time of Contact on Viscosity

From the data on experiments 2 and 3 it is obvious that a short contact time effects viscosity of the bitumen but little. The result of a short time of contact is shown by the point representing experiment 3 on Fig. 4. This point is well above the solid curve obtained at time of contact 100 seconds. At higher temperatures it is probable that there is considerable decrease in viscosity for short times of contact, but the furnaces used would not hold the temperature much above 400°C (temperature of experiment 3 was 393°C) without excessive temperatures and consequent cracking in furnace 1.

Carbon Formation

There was little evidence of carbon formation other than in the form of a suspension in the oil. An accurate determination of suspended carbon was made only for the last three runs. The percentage of carbon for experiment 9 is probably high due to difficulty encountered in filtering. A trend may be seen in Table I. From a value of 0.2% for a "characteristic" temperature 483°C the percentage increases to over 0.5% at 494°C . There is some scale formed in the reactor which does not lose weight with ignition. Scale amounts to less than 0.2% of the throughput of bitumen. Carbon did not deposit in

the receiver in appreciable amounts.

Trend of Sulphur Content

The sulphur content was determined in the last two experiments No. 10 and 11 and on the bitumen feed. The sulphur content is reduced to about 90% of its original value, for these two runs.

Rate of Flow

At time of contact 106 seconds (run #9) the average linear velocity of the oil in the tube was about 0.5 cm. per second. This falls very definitely in the streamline region of flow assuming a Reynold's Number of sixteen as reasonable for the oil in the tube. However, the reciprocating nature of the pump action would give instantaneous velocities much greater than the average and improve mixing and heat transfer. In oil refineries a reciprocating pump is often used to obtain instantaneous turbulent flow in residual oils being treated. Much better heat transfer is possible with turbulent flow, and there is less local overheating. Coke and carbon formation will be much less under these conditions. For a given tube temperature, more extensive vis-breaking should occur with no more, or even less, coke formation than found under conditions of streamline flow.

Distillation Data

All distillations were run at 10 mm. pressure to avoid further cracking or polymerization, except where very light fractions were present. The cracked bitumen containing light products was distilled until the vapor temperature reached about 100°C (700 mm. of mercury). Even at this temperature some sort of mild reaction occurred.

Using an end point of 400°F (760 mm.) for gasoline, which is equivalent to an A.S.T.M. cut-point of 420°F (760 mm.), the corresponding cut-points, 214°C and 91°C, were obtained for pressures of 700 mm. and 10 mm. of mercury, respectively. Referring to Fig. 5, the distillation curve for the original bitumen shows no gasoline present. A maximum of 7.8% gasoline was obtained in experiment 11 at 400 psi.

It may be of interest to note the distillation curves for experiments 1, 3 and 8 are above the curve for the original feed stock. However, the viscosities are less than for the original bitumen (Table I). This suggests some polymerization or condensation reaction. For example, a paraffinic side chain of a naphthene may break, yielding a low molecular weight paraffin (which reduces the viscosity) while the side chain left on the

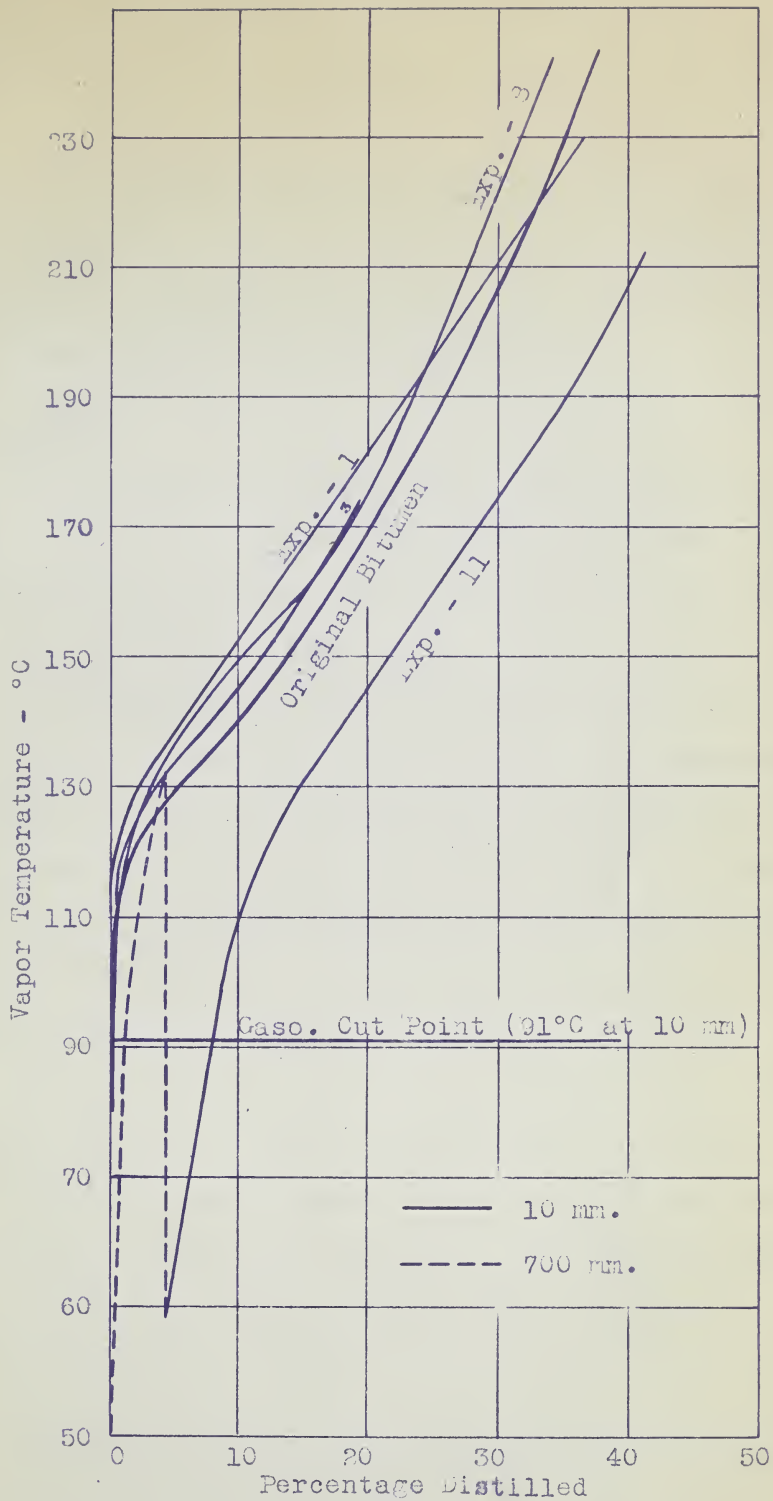


Figure 5 - Distillation Data

naphthenic ring becomes olefinic in nature. This may then polymerize with another similar ring, or, alkylation may occur with a paraffin side chain. This type of mechanism could explain the curves obtained.

Gas Production

Considerable gas formation is associated with cracking and even in some of the present experiments there was a considerable yield of gas. Unfortunately only data for two runs at 200 pounds per square inch are available. Rate of gas production at 494°C was approximately 360 ml. per minute and at 460°C was 300 ml. per minute corresponding to 33 ml. and 29 ml., respectively, per millilitre of bitumen feed. As expected, these figures show more gas formation with higher tube temperature at constant pressure. It would be expected that less gas production takes place at a higher pressure.

The gas produced contained considerable quantities of hydrogen sulphide. This tends to lower the sulphur content of the bitumen. There is also a possibility that gas production agitates the bitumen in the reaction tube, leading to turbulent flow and better heat transfer.

Errors

The error in temperatures should not be great. The characteristic temperature is probably only valid for

comparative purposes with the present apparatus. Errors in density, viscosity and pressure are insignificant when compared to the possible error in the volume of the bitumen charged. The weight of oil recovered should be within five grams of the weight of bitumen fed to the reaction tube. This represents an error of one percent in both the volume and time of contact. It may be concluded that as a whole errors are not great.

CONCLUSIONS

Considerable reduction in viscosity of bitumen has been obtained without excessive coking at 475°-500°C for a time of contact 100 seconds and pressure 200 pounds per square inch. These conditions compare favorably with commercial vis-breaking conditions for a residual oil. No time of contact could be found for any process described in the literature, but temperatures of 460° to 485°C and pressures 200 to 500 pounds per square inch gauge are recorded.

A troublesome problem, that of coking and suspended carbon in the cracked product, might be encountered. At high temperatures, 490°C and above, considerable coke is formed in the tube. However, as previously stated, if turbulent flow were established and if a pressure 300-400 pounds per square inch were used, the coke formation should be minimized. There is considerably less coking at lower temperatures, 475 to 485°C. To compensate for the lowering of temperature a longer time of contact and turbulent flow might be used.

The sulphur content of the bitumen decreases upon being cracked, but the reduction is not great enough to solve the problem of its removal. It is of interest in future work to examine the product of vis-breaking from the point of view of the nature of the sulphur compounds present.

The gases evolved contain hydrogen sulphide and hydrogen but in the main consist of methane and ethane.

While it is difficult to base recommendations on the preliminary data obtained, it may be well to indicate approximate conditions for viscosity breaking of Alberta bitumen. A temperature of 485°C, pressure 400 pounds per square inch gauge, and contact time 150 to 200 seconds appears sufficient to reduce the viscosity of bitumen to less than one tenth its original value, without excessive coke formation.

In future laboratory experiments of this type, a different design of reaction tube and furnace should be employed. The tube should be longer (and/or of smaller diameter) so as to enable the use of high rates of flow simultaneous with times of contact in excess of 100 seconds. The heating arrangement should be such as to produce more uniform temperature distribution along the tube and with respect to time. As an alternative, rather than a tube furnace, a type of reaction chamber might be employed with mechanical agitation to ensure temperature uniformity. This may be a simpler and more satisfactory operation on a laboratory scale.

SUMMARY

A method of reducing viscosity and gravity of Alberta bitumen on a laboratory scale by thermal treatment (vis-breaking) has been described using temperatures 475 to 490°C, pressures 100 to 400 pounds per square inch gauge, and time of contact approximately 100 seconds. Recommendations for future work have been made.

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PART II

THE OXIDATION OF THE PARAFFIN HYDROCARBONS

INTRODUCTION

The controlled or slow combustion of methane to yield useful intermediate products as formaldehyde has received attention by many workers and reports date from 1861. During the decade beginning 1920 a considerable amount of work was reported describing various attempts to produce formaldehyde commercially by the partial oxidation of methane or high methane natural gases. Results were rather discouraging and virtually all such experimental work stopped about 1931.

Early in the present war, however, there occurred a large demand, not only for formaldehyde, but also for methanol, the hithertofore plentiful raw material for the manufacture of formaldehyde. Owing to scarcity of materials for construction of high pressure plants it became apparent that increased production facilities for methanol (basis of formaldehyde manufacture) could not be provided at the rate demand was increasing. In 1941, therefore, under sponsorship of the National Research Council of Canada a program of further research on the oxidation of high methane natural gas, at or near atmospheric pressure, with a commercial application in view, was instituted. Alberta has plentiful and cheap supplies of natural gas to serve as raw material.

Blair and Wheeler⁽³⁾, Ledbury and Blair⁽¹³⁾, have shown high conversions of formaldehyde based on methane consumed, but yields per pass on total methane were discouragingly low.

However, processes utilizing the propane, butane and pentane fractions of wet gases have been developed whose origin may be traced to the pioneer work of the Phillips Petroleum Company. Such processes are operated on a commercial scale by the Celanese Company and Cities Service Oil Company, in the United States of America. In these processes using stabilizer gas, a complex mixture of alcohols, aldehydes and acids is formed. Many useful products such as formaldehyde, acetaldehyde, acetone, ketones and acids, are recovered. Owing to the large demand for butanes and pentanes in the manufacture of aviation gasoline, the extent to which these processes can expand is limited.

In view of the relatively larger and easier supplies of methane as compared to stabilizer gas, the present work was instituted and designed to explore anew effects of temperature, time of contact, etc., upon the overall yield of formaldehyde in an attempt to increase this yield to at least 3 or 4% per pass. It was felt, however, that even with this yield, the large scale pro-

duction of formaldehyde by oxidation, at atmospheric pressure, of methane would only be feasible provided:

1. that a method of concentration involving reaction of gaseous ammonia with the dilute gaseous formaldehyde to produce solid hexamethylenetetramine (hexamine) could be developed; or
2. that countercurrent scrubbing of the dilute gaseous formaldehyde with ammoniacal liquor could be developed to a point where hexamine could be obtained by simple evaporation of the concentrated liquor; or
3. that the dilute gaseous formaldehyde could be made to polymerize to solid paraformaldehyde thus permitting its convenient removal in a concentrated form from the gases.

Otherwise it was felt an investigation of the possibilities at moderate pressure (200-300 pounds per square inch) should be made.

This thesis presents preliminary results concerning the use of commercial oxygen as the oxidizing agent and silica surfaces in the reactor. Owing to the fact that the first objective, i.e., a 3 or 4 percent overall yield of formaldehyde, was not attained the remaining objectives were not attempted.

THEORETICAL AND LITERATURE REVIEW

The objectives of past investigations have been twofold; the first, to establish a mechanism for oxidation of paraffin hydrocarbons, and second, to produce formaldehyde and other products on a commercial scale through the oxidation of methane or high methane natural gases. The latter objective has also promoted many investigations using catalysts for the oxidation.

Mechanism of the Reaction

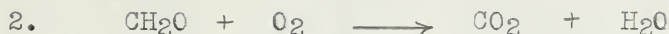
Early theories of the oxidation of methane postulated preferential oxidation of the hydrogen atoms and the formation of carbon and water as primary products. However, carbon was never found. The reverse of this, i.e., the preferential oxidation of the carbon to carbon monoxide before the hydrogen is attacked, was proposed by Kersten⁽¹¹⁾ in 1861. This involves for stable hydrocarbons, the barely credible splitting of hydrogen atoms from the carbon atom.

From circulation experiments with methane and oxygen at 450-500°C, Bone and Wheeler⁽⁴⁾ in 1902 obtained carbon monoxide, water and traces of formaldehyde, but no free carbon or hydrogen. They tentatively concluded that although the overall reaction was probably best represented

by:

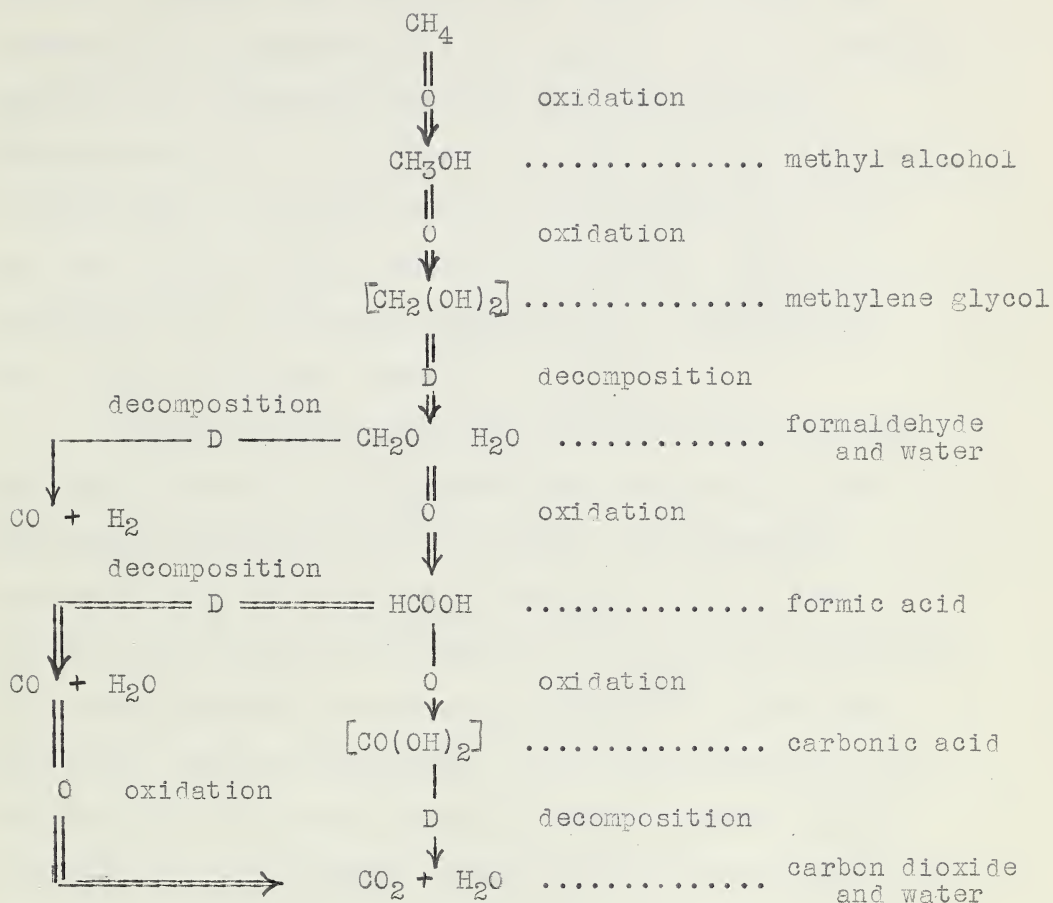


the actual reaction occurred in two steps:



As a result of this work, Armstrong⁽¹⁾ postulated his hydroxylation theory involving the necessary presence of water in combustion of methane. His mechanism involved formation of hydrogen peroxide as one of the primary products. Both the necessity for presence of water and for formation of hydrogen peroxide have since been disproved.

Culminating extensive work by himself and various co-workers⁽⁵⁾, Bone⁽⁷⁾ in 1906 put forth his hydroxylation theory for the mechanism of hydrocarbon oxidation. This theory postulates the stepwise formation of hydroxyl compounds each of which may undergo further oxidation or decomposition by loss of water. The application of this theory is shown on the next page.



Double lines show the usual course of the reaction
 Compounds which have not been isolated are shown in square
 brackets.

The general mechanism by Bone may be sketched briefly. Except for acetylene, the initial product on oxidation of a hydrocarbon is an alcohol. This is further oxidized to a dihydroxyl alcohol which may undergo decomposition to an aldehyde or be again oxidized to yield a fatty acid. The fatty acid is then oxidized to a dihydroxyl compound which usually decomposes. Secondary reactions such as thermal decomposition, condensation, etc., are, of course, possible.

Despite diligent search, Bone failed to isolate methanol as one of the intermediates. This was one of the serious weaknesses in his theory. The accepted explanation for the absence of methanol is that for temperatures in excess of 300°C it is completely decomposed to carbon monoxide and hydrogen, Kelley⁽¹⁰⁾, Smith and Hirst⁽¹⁹⁾, Bone and Davies⁽⁶⁾. Also questionable is the necessity for oxygen to behave as atomic oxygen and for the atom to insert itself between carbon and hydrogen, or alternatively for the occurrence of a termolecular collision in the first steps of the reaction.

In opposition to Bone's Hydroxylation Theory, is Stephen's⁽²¹⁾ Hydroxylation Theory. It postulates, that since the presence of water retards progress of the oxidation reaction, the reaction conceivably involves

splitting out of water as a product.

Thus:



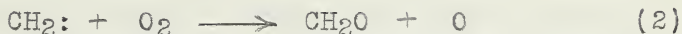
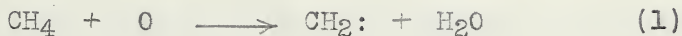
which then undergoes a molecular rearrangement to give formaldehyde and water:



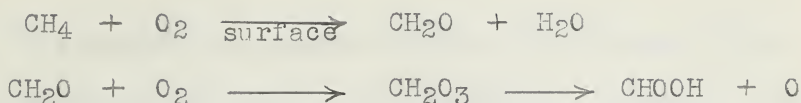
In favor of this mechanism is its simplicity; it involves molecular oxygen and a bimolecular collision. Any methanol formed would occur as a by-product rather than as an intermediate.



A recent modification of the first step of Bone's theory has been proposed by Norrish⁽¹⁷⁾ in his Atomic Chain Theory. He assumes the initial step to be:



The reaction is presumably initiated by oxygen atoms supplied through the oxidation of formaldehyde originally found on the reactor walls according to:



while the formation of oxygen atoms is not questioned it has never been proved satisfactorily that the methylene radicle exists⁽²⁰⁾ and it is essential to this mechanism.

Boomer and Thomas⁽⁹⁾ combined features of Bone's Hydroxylation Theory and the Chain Theory of Norrish to explain formation of methanol obtained at high pressures. Two primary reactions are suggested, a surface reaction between methane and oxygen and a homogeneous gas phase reaction. Both reactions require activated oxygen; in the first, oxygen may be adsorbed on the catalyst surface (or combined with the catalyst) and in the second, oxygen may be activated or in the atomic form. The surface reaction may be written as follows:



The methanol formed may survive or proceed to formaldehyde or formic acid according to Bone's mechanism through further oxidation. This reaction is thought by Norrish to play the role of a chain breaker. The homogeneous reaction may be taken from Norrish's initial step (Equations (1) and (2)). This is a chain reaction and it may be

broken by equation (3) above. Glass and silica, which promote aldehyde formation, at atmospheric pressure, may not act as catalysts but may break the chains efficiently in Norrish's reaction.

In 1936 Bone and Gardener⁽⁸⁾ and Newitt and Gardener⁽¹⁶⁾ identified, by careful experimental procedure, methyl alcohol as one of the by-products in the oxidation of methane at atmospheric pressure. They found small quantities of both methanol and formaldehyde in the induction period, at temperatures from 390°-420°C, and in the reaction period. At a temperature of 390°C slow oxidation of methanol was much faster than that of methane. The methanol reacted to give water, carbon monoxide and carbon dioxide. The ratio of alcohol to aldehyde decreased as the induction period approached completion, which would indicate alcohol formation prior to aldehyde formation, as would be expected by the hydroxylation theory.

As a result of this work they postulate that the initial stage of oxidation is a slow reaction occurring at a surface, but it becomes homogeneous in later stages. They state, "if eventually a chain mechanism has to be involved it should be one involving the primary formation of methyl alcohol". The theory advanced by Boomer and

Thomas⁽²²⁾ seems to satisfy experimental work by the latter workers.

Formaldehyde Production

Extensive work was done with a view toward formaldehyde production during World War I by Blair and Wheeler⁽³⁾ but it was not reported until 1923. They used carefully purified methane mixed with oxygen in a circulatory system similar to the one in which Bone and Wheeler⁽⁴⁾ had earlier detected formaldehyde. This work was extended over a temperature range of 665° C to 740°C, with oxygen concentrations varying from 6.3% to 86.9% and heating periods of 0.8 to 3.2 seconds. They conclude, "A short time of heating and a slow oxidation are the principle factors in obtaining a good yield of formaldehyde. If the oxidation is vigorous it (the formaldehyde) is formed in such a large proportion that it rapidly decomposes. A long time of heating has similar effects."

A maximum yield obtained by Blair and Wheeler, while reported as 2.9 mg. of formaldehyde per litre of gas mixture is equivalent to 0.4% of the theoretical based upon the methane input, or 19% based upon the methane burned. This was obtained at 720°C with a heating time of 1.0 second.

Tropsch and Roelen⁽²³⁾, using a 1:1 mixture of methane to oxygen, a heating time of 1/1,000 second, and a temperature of 1,000°C obtained a maximum yield of 5.96% of the theoretical formaldehyde. This temperature is probably excessive from a commercial point of view.

Ledbury and Blair⁽¹³⁾ also reported work that had been carried out during World War I to obtain a commercial process for the oxidation of methane to formaldehyde. Their results are similar to those of Wheeler and Blair and they recommend an operating temperature of 700°C and a heating time of about 0.8 seconds with pure oxygen. They have also presented a proposed layout for a commercial plant employing recirculation of the gases. However, they point out "The oxidation on a technical scale for the manufacture of formalin can only be considered as an economic proposition if methane is obtainable in quantities at low or even nominal cost". This may even be an overstatement of the fact.

A large amount of work has been done by various investigators upon the catalytic oxidation of methane to formaldehyde. Many catalysts have been used, such as metals and metallic oxides, but it appears that the equilibrium is carried to completion and only minute traces of formaldehyde, etc., are found. Blair and Wheeler

sum up the reason for failure as follows:

"This (the failure to produce formaldehyde) is not surprising. The formaldehyde obtained in our circulation experiments is in a concentration much greater than given by the equation:



The rapid cooling enables it to be isolated before equilibrium is attained or further oxidation can occur. But with catalysts the true equilibrium is attained almost instantly at the temperatures necessary to oxidize methane."

With a mixture of phosphates of tin, iron and aluminum, methane in the presence of hydrogen chloride decomposed to the extent of 6.7% of which one half was formaldehyde⁽¹⁴⁾.

Much work has been done on the effects of the nitrogen oxides upon the slow oxidation of methane. Layng and Soukup⁽¹²⁾ obtained a 38% decomposition of methane per pass, with a conversion of 11% largely to formaldehyde but some methanol. Bibb and Lucas⁽²⁾ obtained a 4% conversion (based upon methane input) to formaldehyde at 700-750°C and a heating time of less than 0.5 seconds.

In 1931 after extensive work Smith and Milner^(19a) concluded that it was not feasible to use the nitrogen

oxides as a catalyst commercially. They pointed out that very little or none of the oxides used could be recovered and this from the economic point of view is objectionable.

MATERIALS

Commercial oxygen as supplied in cylinders was used as the oxidant. A high methane natural gas from the Viking-Kinsella field was used as the paraffin hydrocarbon source. The gas was scrubbed with concentrated sodium hydroxide to remove carbon dioxide and some, or all, of the sulphur odorant.

The approximate analysis of this gas by a low temperature-low pressure fractional distillation was as follows:

92.3%	methane
2.4	ethane
0.6	propane and higher
<u>4.7</u>	nitrogen
100.0	

Throughout this project it has been found convenient to consider the natural gas as methane plus nitrogen and to report the hydrocarbon in terms of methane having the equivalent carbon content of the total hydrocarbon in the gas.

APPARATUS

The apparatus for oxidation of methane by oxygen was designed for the continuous and uniform flow of a mixture of oxygen and natural gas through a reactor held at constant temperature, for a predetermined time of contact. Condensable products and water soluble products were recovered from the off-gas and estimated by weighing and analysis. Proportional samples of both in-gas and off-gas were taken throughout each experiment. A detailed description follows.

The gas oxygen mixture was prepared and stored in the 20 cubic foot, water sealed, gasholder, A, Figure I. The small compressor, B, fed the mixture to the high pressure storage, B¹, thence to a reducing valve, C, and the surge tank, D. The pressure in the surge tank, D, was maintained at 20 centimeters as indicated on the mercury filled manometer, E, by an automatic pressure control operating the compressor, B. Constancy of rate of flow in the reactor system was obtained by adjustment of the needle valve, F, only if the pressure in tank, D, were steady.

The gas was dried in the calcium chloride-magnesium perchlorate filled drying tower, G₁, and measured in the oil filled wet-test meter, H, operating under system pressure of a few centimeters of mercury.

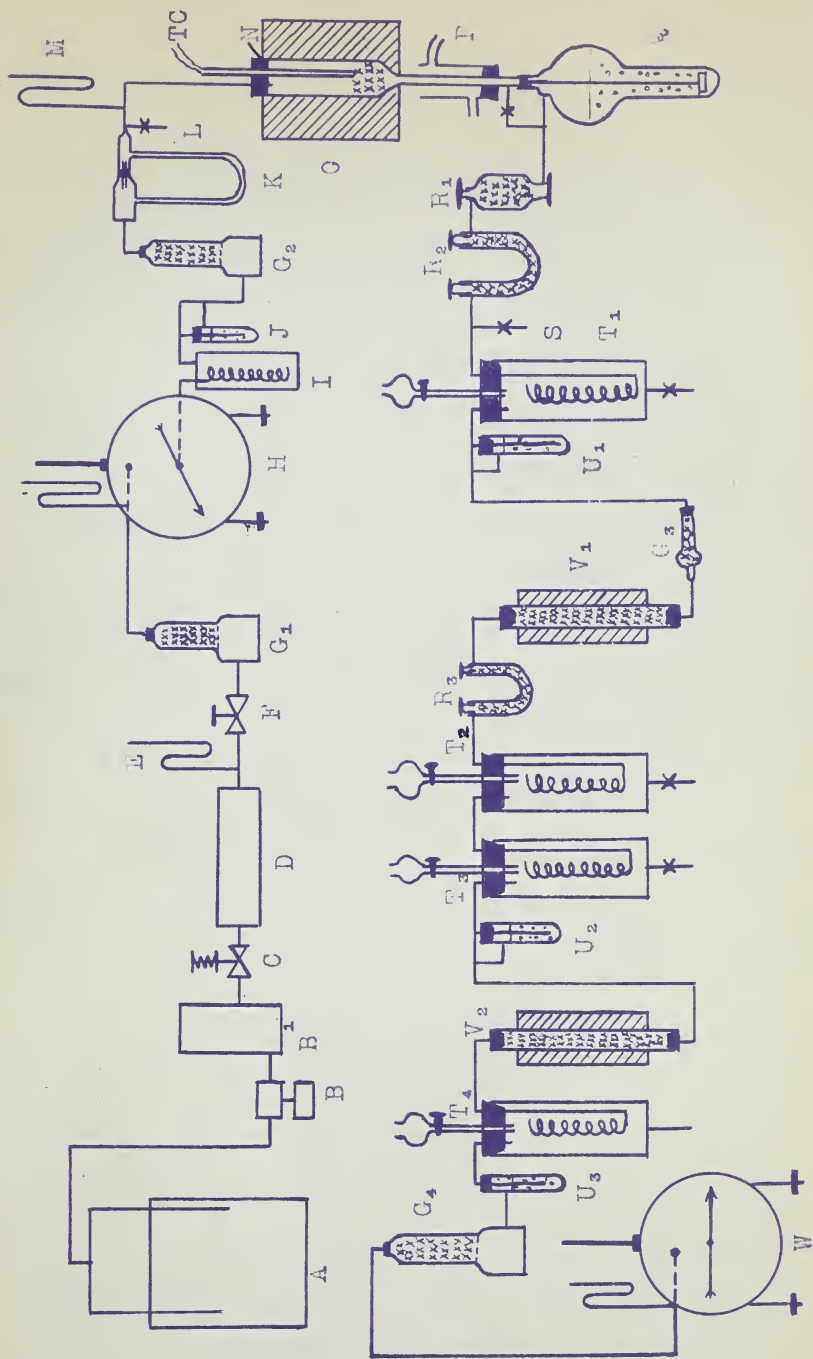


Figure 1 - apparatus for Oxidation of Methane

After being metered, the gas was scrubbed in I with concentrated potassium hydroxide, dried again in tower G₂. The absence of carbon dioxide in the in-gas was indicated by calcium hydroxide bubbler, J. The rate of flow of in-gas was indicated by the capillary flowmeter, K. The flowmeter limbs contained water as manometer fluid. A continuous in-gas sample was taken at L, throughout each run. The reactor pressure was indicated by manometer, M. The reactor, N, of quartz tubing was heated by furnace, O, the temperature of which was indicated by means of a platinum-platinum rhodium thermocouple and controlled automatically at the desired temperature. The condenser, P, attached to the lower part of reactor, N, cooled the gas immediately after leaving the reactor.

The water soluble constituents of the gas were scrubbed in a fritted glass scrubber, Q, placed in an ice bath. The drying tower, R₁, and guard drier, R₂, contained magnesium perchlorate and collected all moisture from the gas. The scrubber and driers were of such design that they could be weighed accurately on an analytical balance. The proportional off-gas sample was taken at S. Carbon dioxide was scrubbed quantitatively in the scrubber, T₁, containing standard potassium hydroxide solution. The complete removal of carbon dioxide was

checked by means of a calcium hydroxide bubbler, U_1 .

The low concentration of carbon monoxide and hydrogen in the off-gas made precise analysis by the usual Orsat methods impossible. Hence, soon after the start of experiments, a copper oxide furnace, V_1 , maintained at $290-300^{\circ}\text{C}$, was added, in which carbon monoxide was oxidized to carbon dioxide. A drier, R_3 , after the furnace, allowed an accurate quantitative measurement of hydrogen in the off-gas. Two alkali scrubbers, T_2 and T_3 , allowed a quantitative determination of carbon dioxide (hence carbon monoxide). This was followed, as usual, by calcium hydroxide bubbler, U_2 .

In order to ensure complete removal of carbon monoxide a second copper oxide furnace, V_2 , was added, and followed by alkali scrubber, T_4 , and bubbler, U_3 (similar to previously described copper oxide furnace and train), was installed. The off-gas then passed through a drier, G_5 , before being metered by wet-test meter, W .

A further modification for carbon monoxide determination was made for runs 55 and 56 by insertion ahead of copper oxide tubes, of a Hopcalite catalyst placed in three U-tubes, and heated to the appropriate temperature by means of an oil bath. The Hopcalite was made

following the method of Merrill and Scalione⁽¹⁵⁾, and consisted of 60% manganese dioxide and 40% copper oxide.

It was found that oxidation of hydrocarbons over the copper oxide and over Hopcalite took place to a small extent. As a consequence, after run 58, both the Hopcalite catalyst and copper oxide tubes were abandoned and the off-gas was analysed by the usual Orsat methods using an improved type Bureau of Mines apparatus.

The reactor and catalyst were the same as used in previous work on the oxidation of high methane natural gas by air. A detailed description follows.

The main part of the reactor was a 7/8" O.D. x 7" long silica tube. This was fused, at the bottom, to a piece of 1/4" O.D. x 9" long silica tube. A short condenser was attached near the top of the 1/4" silica tube. The catalyst consisted of broken silica screened to 3/16" to 1/4" size. The volume of silica was 5.65 ml. and surrounding free space 11 ml. A two holed, air cooled, rubber stopper introduced the gas mixture and a thermocouple well to the reactor. The thermocouple well reached the catalyst bed.

ANALYTICAL PROCEDURE

The weight of water and water soluble products formed in the oxidation process, was determined by weighing scrubber, Q, Figure I, and driers, R₁ and R₂, before and after a run, on an analytical balance.

Determination of Formaldehyde

The volume of the scrubber liquid, Q, was found, after which a quantitative formaldehyde determination was run on a 10 ml. aliquot following the method of Romijn⁽¹⁸⁾ as modified by Thomas⁽²²⁾.

To the aliquot was added 10 ml. of N/10 potassium cyanide solution, enough to ensure an excess of potassium cyanide. The formaldehyde combines with the cyanide to form a soluble addition compound, as follows:



This mixture was added to 15 ml. of N/10 silver nitrate solution, acidified with concentrated nitric acid, whereupon the excess potassium cyanide precipitated out as silver cyanide.



The precipitate was immediately filtered off and the diluted filtrate titrated with N/20 potassium thiocyanate solution, using ferric alum as indicator.

The amount of formaldehyde was calculated as the chemical equivalent of the difference between potassium thiocyanate used in a blank analysis and that used in titrating the filtrate from a run.

For the first few runs Schiff's fuschin-aldehyde reagent was used to determine qualitatively the presence of formaldehyde. A pink color is observed even with minute amounts of formaldehyde.

Determination of Formic Acid

No formic acid was found in any run.

Gas Analyses

An improved type Bureau of Mines Orsat gas analysis apparatus was used for all in-gas, and some off-gas analyses. Carbon dioxide, oxygen, carbon monoxide, hydrogen and total carbon were determined in the proportional gas samples.

A more accurate determination of carbon dioxide was obtained by titration of the contents of the alkali scrubbers. The scrubbers were charged with known volumes of 3N standard alkali and the titration was carried out

with N/2 standard sulphuric acid using methyl orange as indicator.

Carbon monoxide was determined for experiments 40-51, inclusive, by oxidation to carbon dioxide in copper oxide tubes followed by standard alkali scrubbers. The carbon monoxide is equivalent to the amount of carbon dioxide determined in these scrubbers.

After the copper oxide and before the alkali scrubber, a drier, which could be weighed accurately, collected water formed by oxidation of hydrogen in the off-gas. A quantitative estimation of hydrogen was thus made.

Much time and effort was spent in developing the use of copper oxide as a method for preferential oxidation of carbon monoxide and hydrogen in the presence of oxygen and lower paraffin hydrocarbons. The attempt was discontinued when it became evident that there was always some oxidation of paraffin hydrocarbons under any conditions that gave oxidation of carbon monoxide and hydrogen. Consequently in all experiments where copper oxide alone was used to analyse off-gas, there are not reliable data on the off-gas, except as to carbon dioxide content.

EXPERIMENTAL PROCEDURE

The furnace, O, Figure 1, was turned on prior to the start of a run and the automatic controller was set to the desired reactor temperature. When copper oxide tubes were used, the furnaces heating them were turned on at the same time. Meanwhile scrubber, Q, Figure 1, was filled with distilled water and weighed accurately. Driers R₁ and R₂, and when copper oxide tubes were used, drier R₃, were weighed. Scrubber T₁, and when used, T₂ and T₃, were filled with a known volume of 3N sodium hydroxide solution. The bubblers following the scrubbers were filled with saturated calcium hydroxide solution. The scrubbers, driers and bubblers were put in place, along with the proportional gas samplers.

The readings of in-gas and off-gas wet-test meters were recorded along with barometric pressure. When the reactor and copper oxide tubes had reached the desired temperatures the small compressor was started and the pressure in surge tank, D, Figure 1, allowed to build up.

The valve, C, was opened to admit the gas-oxygen mixture to the system and flow was adjusted by means of flowmeter K; the stopwatch was started at the time of opening valve C. Readings of pressure of the in-gas wet-test meter and reactor were taken, as well as temperatures of in-gas, off-gas and the room. These readings

were also recorded at various intervals during the run.

The duration of the run depended on the time of contact chosen and the fact that at least one cubic foot of gas mixture was passed through the reactor.

At the conclusion of the run, valve C was shut and the proportional gas samples were stopped and their volume recorded. The time and wet-test meter readings were taken immediately. Furnaces were shut off and an air stream was started through the apparatus following the same route as the gas mixture. When the reactor connection to the scrubber had been cleared of condensate, the scrubber was by-passed, until connections to driers had been swept dry. The air was then shut off.

The driers and scrubbers were immediately taken off the apparatus and weighed. The contents of alkali scrubbers were drained into erlenmeyer flasks, which were stoppered until analyses were carried out.

EXPERIMENTAL RESULTS AND DISCUSSION

The experimental results are very erratic. The difficulty in reproduction lies partially in the narrow temperature range usable (700°-740°C) and high temperature coefficient of all reactions, primary and secondary. These may be illustrated by the following equations:



Minor changes in temperature and rate of flow have great influence. In addition, the products of interest are produced in relatively small concentrations in the off-gas. The methods of analysis for carbon monoxide and hydrogen, in particular, may have very poor relative accuracy. The usual Orsat methods, good to about 0.1 percent, are not very satisfactory in dealing with components present to the extent of 1 percent or less. These analytical difficulties influence particularly the data on the percentage of methane oxidized ("burned"), and yield of formaldehyde on basis of total methane burned.

In spite of inaccuracy in analytical results, qualitative trends are indicated. Total oxidation of methane increases with time at constant temperature, or

increases with temperature for constant time, as is evident from the data plotted (from Table I) in Figure 2. In addition, it is evident in Figure 2 that, for constant time and temperature total oxidation increases with increasing oxygen concentration, within the limits of work done (5-20 percent oxygen).

The data plotted in Figures 3, 4, and 5 show the yield of formaldehyde (efficiency) on the basis of total methane oxidized. The efficiency increases with decreasing time for a given temperature and probably reaches a maximum value. The efficiency also increases, within the limits of the work, with increasing temperature for a given time and oxygen concentration.

Maximum yield for a twenty percent oxygen mixture (Figure 5) is between the maximum yields for 5 and 15 percent oxygen (Figures 3 and 4), the peak efficiency passing through a maximum with increasing oxygen concentration from five to twenty percent.

For a five percent mixture of oxygen with gas, yield of formaldehyde on throughput of methane (overall yield) passes through a maximum with increased time, for a given temperature, as shown in Figure 6. The comparative curves for fifteen percent oxygen are shown in Figure 7. The maximum in this case corresponds to more than twice

TABLE I. Data for Oxygen Oxidation

Run No.	Time of Contact sec.	% O ₂ In-Gas	Off-gas Analysis				H ₂ O CH ₂ O	% CH ₄ Burned	% CH ₂ O Based on CH ₄ Burned	% CH ₂ O Based on CH ₄ Thru†	Temp. °C
			C O ₂	O ₂	CO	H ₂					
37	1.72	4.6	0.62	-	-	-	12.50	0.66	9.6	0.06	720
38	0.56	4.9	0.32	4.33	0.10	0	6.24	0.49	8.0	0.04	714
39	1.17	4.8	0.46	3.64	0.54	1.28	5.44	1.13	8.05	0.09	720
40	1.91	5.0	0.33	-	1.58#	-	182	0.58	1.79	0.01	720
41	0.56	5.3	0.07	4.36	0.14#	-	4.66	0.28	23.5	0.07	740
43	0.63	14.6	0.06	12.55	0.41#	-	36.7	0.59	7.7	0.05	720
45	1.18	14.6	0.14	11.50	1.51#	0.95#	3.67	2.06	10.2	0.21	720
46	0.47	14.6	0.07	13.55	0.73#	0.63#	7.51	1.06	17.8	0.18	720
47	1.07	15.3	0.10	10.50	3.09#	1.04#	21.1	3.46	6.5	0.23	740
48	1.79	15.3	0.50	8.13	4.60#	2.06#	37.1	4.85	3.84	0.19	720
49	1.40	15.3	0.24	10.98	3.36#	1.31#	17.04	3.80	6.42	0.24	700
50	0.64	15.3	0.03	-	0.29#	0.17#	141.0	0.35	2.42	0.01	700
51	0.73	15.3	0.01	-	1.14#	1.48#	0.80	1.45	15.62	0.23	700
55	0.64	19.7	0.06	17.65	1.60	0.90	8.00	2.30	10.4	0.24	700
56	1.12	19.7	0.20	15.00	3.80	2.00	21.0	4.59	5.70	0.26	700
57	0.62	19.5	0.13	15.70	1.30	2.80	15.6	3.62	6.98	0.25	720
58	0.45	19.5	0.03	17.72	1.52	0.22	7.96	2.00	10.6	0.23	720
59	0.35	19.6	0	19.21	1.89	-	3.41	2.35	2.12	0.04	680
60	0.33	19.4	0.41	12.74	5.60	2.62	10.9	8.08	14.1	1.14	680
61	1.09	18.7	0.09	16.20	2.00	1.08	6.78	2.96	15.2	0.45	720
62	1.00	19.1	0.03	17.97	1.08	0.59	7.11	1.54	13.1	0.20	700
63	0.63	19.1	0.19	18.90	0.37	0.13	1.56	0.84	13.6	0.11	680
64	1.50	19.1	0.08	-	-	-	11.4	-	-	0.19	680

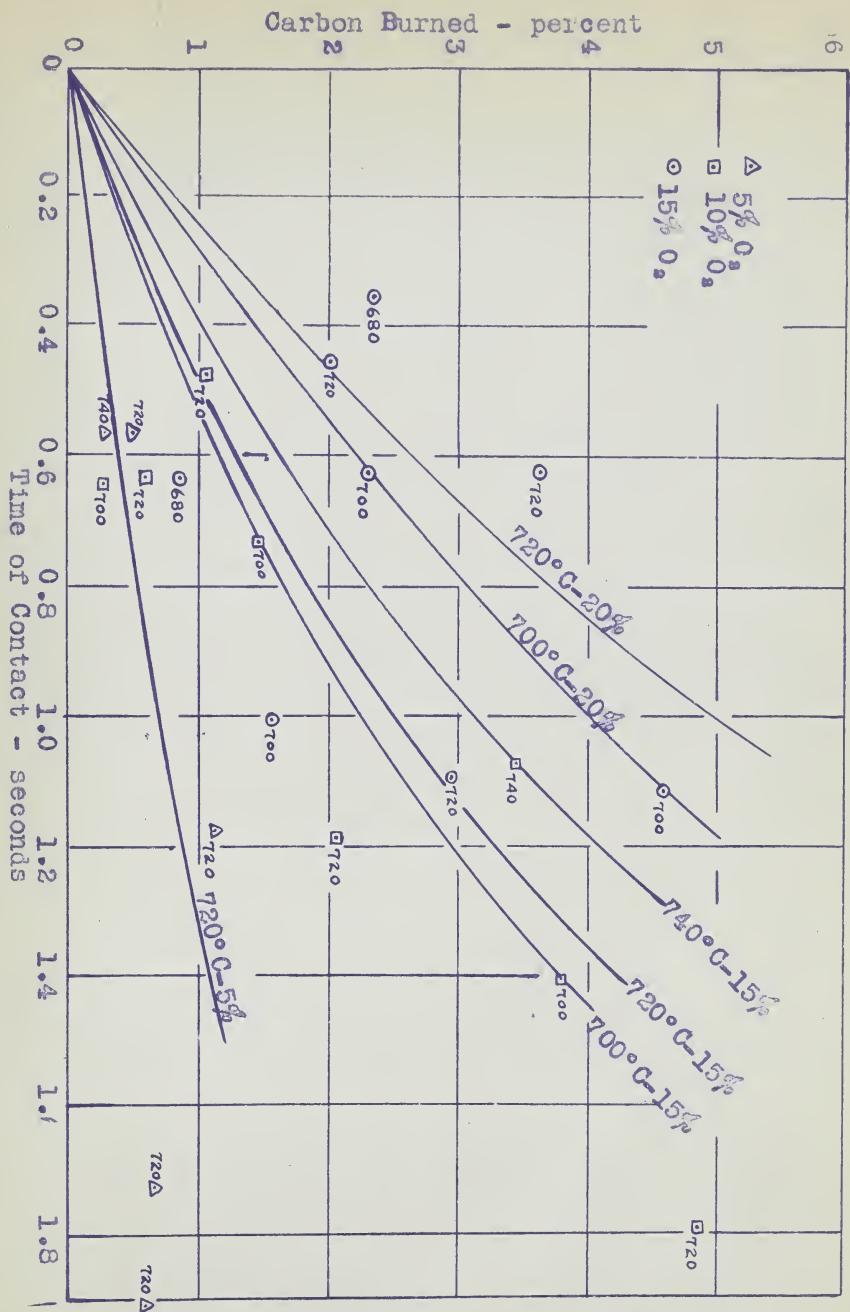


Figure 2 - Effect of Time on Carbon Burned

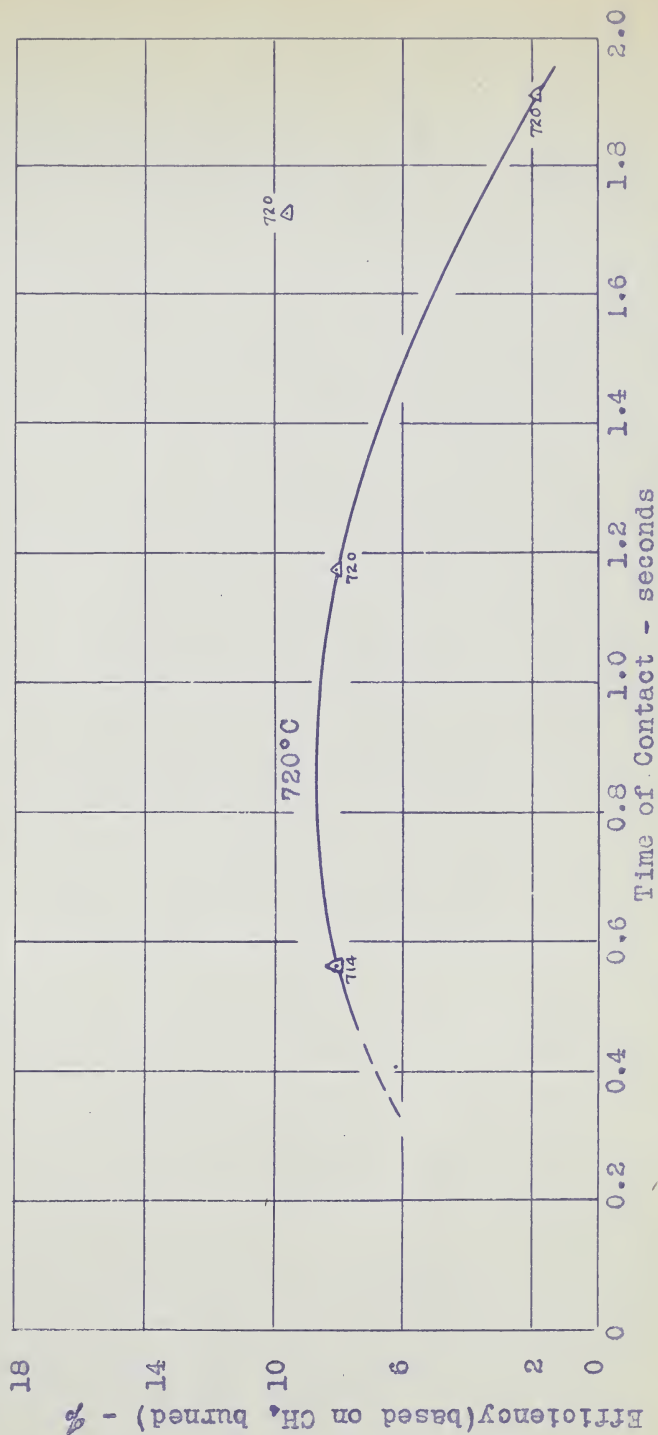


Figure 3 - Effect of Time on Conversion to Formaldehyde (5% O₂)

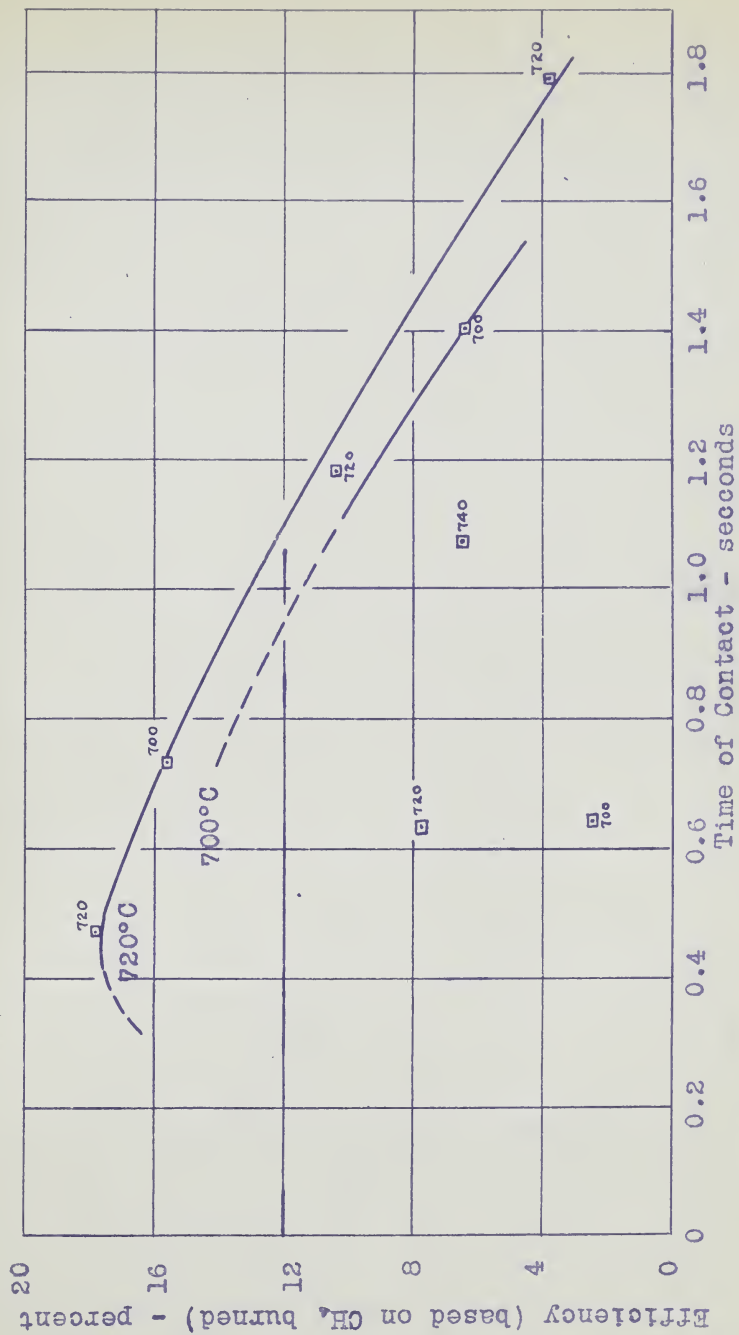


Figure 4 - Effect of Time on Conversion to Formaldehyde (15% O₂)

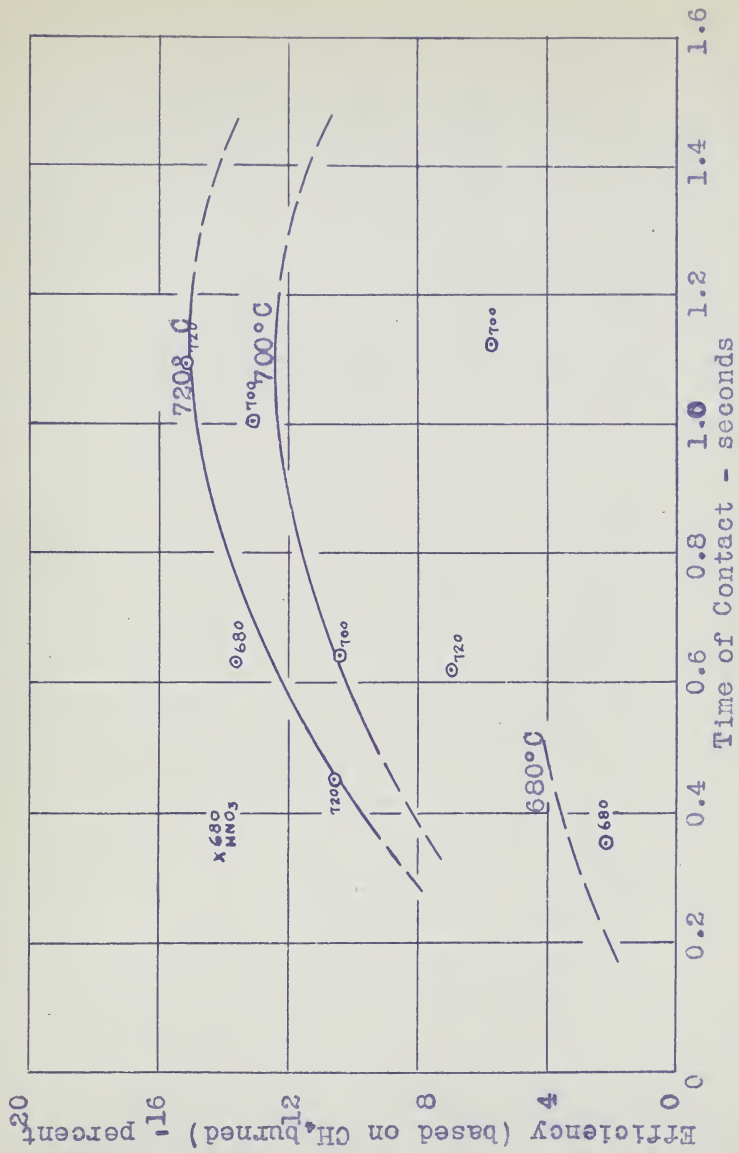


Figure 5 - Effect of Time on Conversion to Formaldehyde (20% O₂)

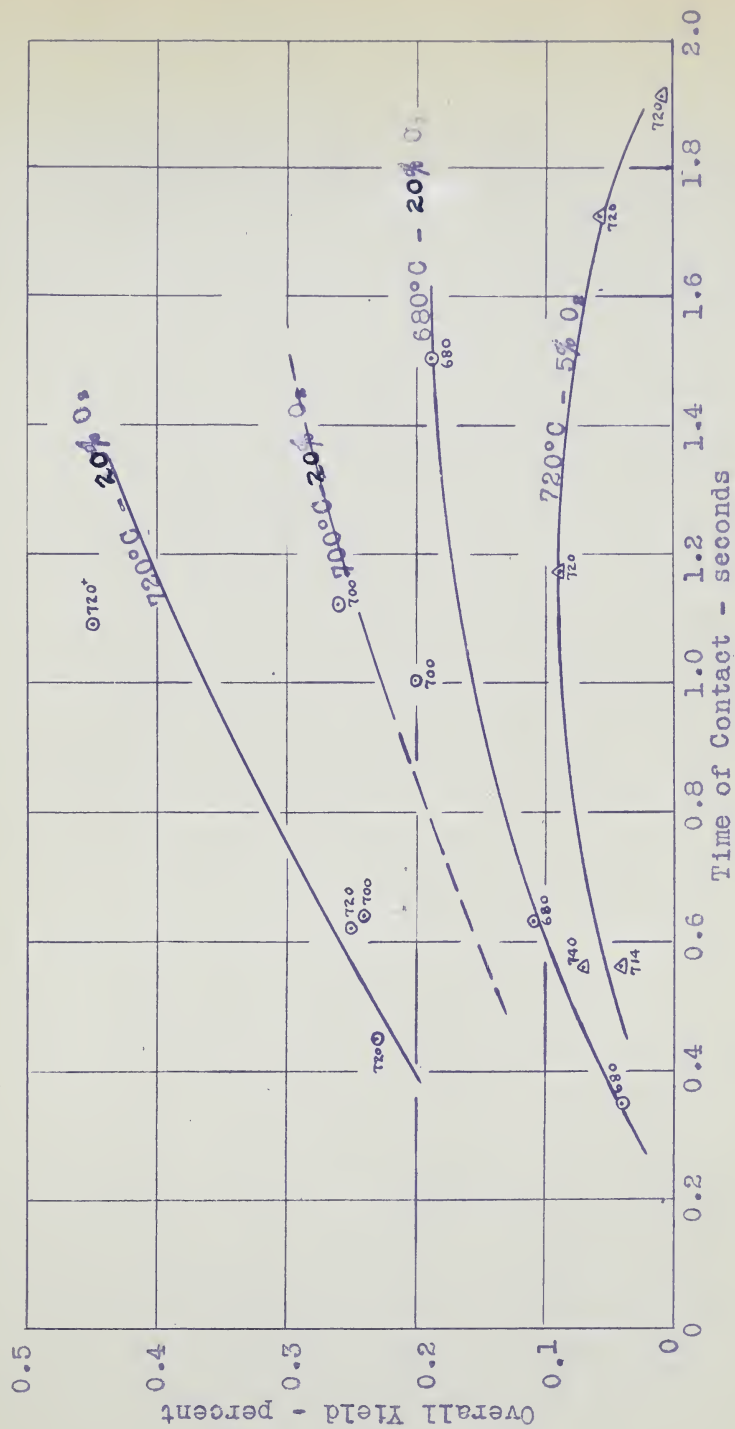


Figure 6 - Effect of Time on Overall Yield



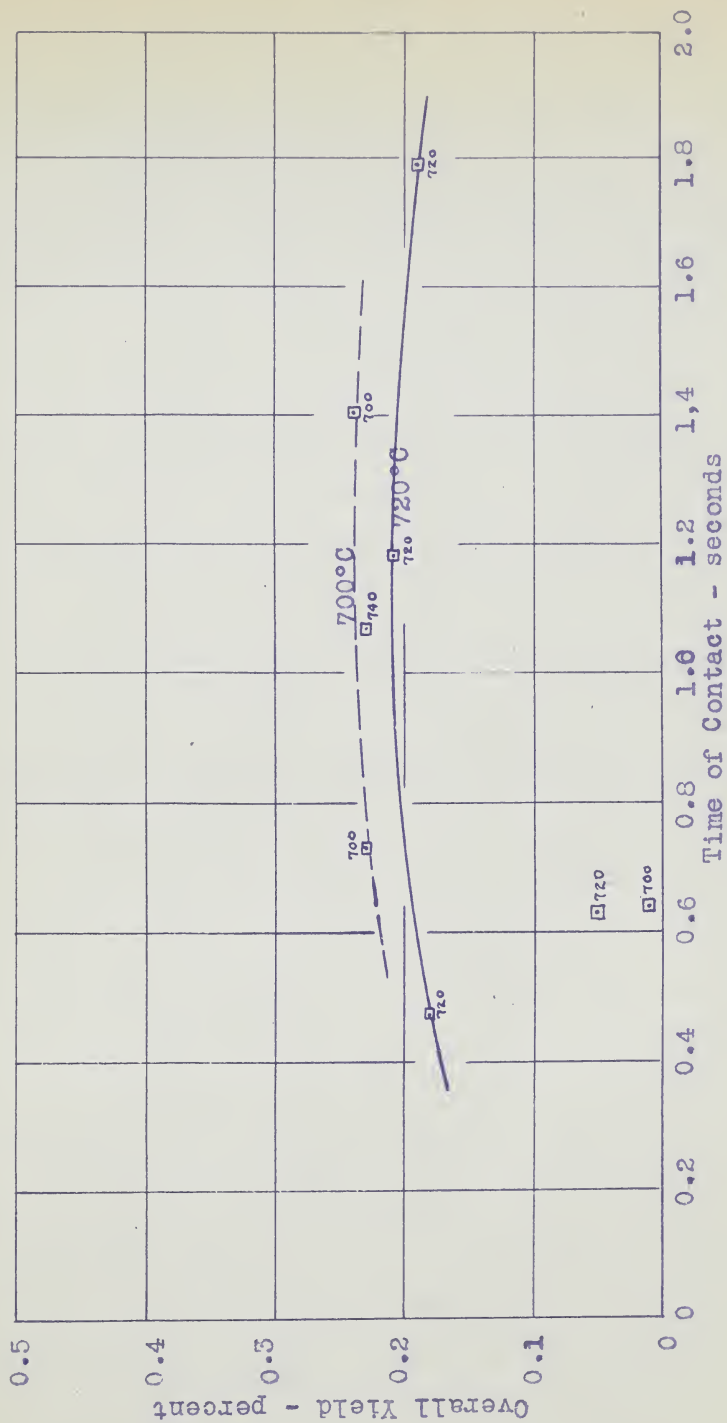


Figure 7 - Effect of Time on Overall Yield (5% ϕ .)

the overall yield as found with five percent oxygen. The same function plotted for twenty percent oxygen, Figure 6, gives a rising overall yield with increasing time. This would suggest that much higher oxygen concentrations might result in higher overall yields of formaldehyde. However, taking into consideration effect of oxygen concentration on efficiency of methane conversion to formaldehyde (a maximum between five and twenty percent oxygen), it is probable that excessive oxidation to valueless products as carbon monoxide, hydrogen and water, would occur with further increases in oxygen concentration. Nevertheless, a higher range of oxygen concentration might be a matter for investigation in future work.

One experiment (#60, Table I) was made with nitric acid vapors as a catalyst, in order to confirm previous work done by Bibb and Lucas⁽²⁾ and others^{(12)(19a)}. The data is plotted in Figure 5 and is marked 680 - HNO_3 . In the presence of nitric acid vapors an efficiency of fourteen percent was obtained as compared to two percent without a catalyst, and similarly an overall yield of 1.1 percent was obtained, as compared to 0.04 percent, under the same conditions of temperature, time of contact and oxygen concentration. All nitrogen oxide was destroyed

in the reactor, confirming Smith and Milner's work^(19a). However, while Smith and Milner found a mol, or less, of formaldehyde produced per mol of nitric acid used, the present experiment showed ten mols of formaldehyde per mol of nitric acid used.

Errors

The quantitative validity of experimental and analytical data may be tested by the method of material balance. It consists of evaluating quantitatively, materials going into and coming out from a system, in order to estimate losses. The present experiments had a gas-oxygen mixture entering the reactor, and gaseous and liquid products leaving the reactor. The method may be demonstrated by using the data from experiment 61.

Material Balance

Experiment 61

In-gas Analysis

% O ₂	18.68
Cl	<u>81.32</u>
	100.00

In-gas = 25.5 l. N.T.P.
Off-gas = 24.9 "

Off-gas Analysis

% CO ₂	0.09
O ₂	16.20
CO	2.00
H ₂	1.08
Cl	<u>80.63</u>
	100.00

Materials In

				gms.		
	%	litres	gm.	<u>O</u>	<u>C</u>	<u>H</u>
O ₂	18.68	4.76	6.81	6.81	-	-
C ₁	81.32	<u>20.74</u>	<u>14.81</u>	-	<u>11.11</u>	<u>3.70</u>
		25.50	21.62	6.81	11.11	3.70

Materials Out

Gaseous

				gms.		
	%	litres	gm.	<u>O</u>	<u>C</u>	<u>H</u>
CO ₂	0.09	0.022	0.043	0.031	0.01	-
O ₂	16.20	4.04	5.75	5.75	-	-
CO	2.00	0.498	0.622	0.35	0.27	-
H ₂	1.08	0.27	0.024	-	-	0.024
C ₁	80.63	<u>20.07</u>	<u>14.36</u>	-	<u>10.77</u>	<u>3.59</u>
		24.90	20.80	6.131	11.05	3.614

Liquid

H ₂ O	-	-	0.847	0.753	-	0.094
CH ₂ O	-	-	0.125	<u>0.067</u>	<u>0.05</u>	<u>0.008</u>
Total Output - gm.				6.951	11.10	3.716
Total Input - gm.				6.81	11.11	3.70
Percent error (basis input)				2.1	0	0.4

A very good material balance results in experiment 61, especially the carbon balance. However, many experiments showed poorer material balances than did the example chosen.

A material balance will not show error in analytical method such as occurred in many experiments, in the present work, by use of copper oxide to estimate carbon monoxide and hydrogen. This error has been described previously. All products resulting from oxidation by copper oxide were estimated quantitatively by titration of the alkali scrubber liquid, so no large error resulted in the material balance. However, an error occurred when using this result to estimate total methane burned. The experiments liable to error by this means are marked (#) in Table I.

To avoid an error in overall yield the estimation is based upon formaldehyde formed and gas entering the system, in experiments where copper oxide was used for the off-gas analyses. In all other experiments the overall yield is the product of percentage of methane burned, based upon Orsat analyses, and fraction of conversion to formaldehyde.

CONCLUSIONS

Yields are low but compare favorably with Blair and Wheeler's work⁽¹⁾. Their best overall yield was 0.4 percent (19.4% efficiency) at 720°C and one second contact time with a 49.4 percent oxygen-methane mixture, using small quartz tubes, whereas, using the plotted data (Figure 6) and interpolating, the present experiments show overall yield of 0.4 percent (14% efficiency) at 720°C and 1.3 seconds with a 20 percent oxygen-gas mixture. Higher yields were obtained in individual experiments.

No yield of commercial interest was obtained from oxidation at atmospheric pressure.

SUMMARY

Oxidation of high methane natural gas by oxygen has been carried out on mixtures containing 5, 10, and 15 percent oxygen, at temperatures 680^o to 740^oC and times of contact 0.3 to 1.9 seconds. Overall yields (based on methane through) were of the order of 0.1% and attained a maximum of 0.45%, while efficiency (formaldehyde formed from methane burned) varied from 2 to 15 percent. No yield of commercial interest was obtained.

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